ACRYLIC-METHYLENE SUCCINIC ESTER EMULSION COPOLYMERS FOR THICKENING AQUEOUS SYSTEMS

This application is a continuation-in-part of application Ser. No. 782,571 filed Oct. 1, 1985, which in turn is a continuation-inpart of application Ser. No. 719,768 filed Apr. 4, 1985, now abandoned.

BACKGROUND OF THE INVENTION

Alkali soluble and alkali swellable emulsion polymers and copolymers are well known (see e.g. Pat. Nos. 3,003,987; 3,070,561, and 3,081,198) and are useful in coatings, textile sizings, textile printing pastes, paints and industrial coatings where a water soluble resin can be utilized. They are also useful as thickening agents in latex based adhesives, where clays, other fillers, pigments and the like are present. In addition, alkali soluble emulsion polymers and copolymers find application in cleaners, laundry detergents, lotions and other personal care products. In petroleum exploration, acrylic polymers are used as drilling fluid additives for viscosity control and as bentonite extenders for enhancing performance of the drilling fluid. Thus, according to U.S. Pat. No. 4,301,016 water soluble alkali metal polyacrylates are useful additives in drilling fluids based on fresh water.

In drilling muds acrylics have performed well in fresh water drilling, U.S. Pat. No. 4,301,016, supra, and U.S. Pat. No. 2,718,497, but acrylics have poor salt tolerance as compared to some cellulosic materials. On the other hand acrylics and other synthetic polymers and copolymers offer a major advantage in manufacturing reproducability, as compared to chemically grafted or modified natural products, provided the salt tolerance problem is not a factor.

The resistance of acrylic polymers to biological decay is a property which is especially beneficial in drilling muds, paints, cleaner solutions, and personal care products. In order to provide improved properties for specific applications, functional polymeric side chains have been added to synthetic acrylic systems.

In various industrial applications, acrylics available as liquid emulsions and dispersions are generally easier to use than modified natural polymers which usually are dry powders, since the former are capable of addition at most any point in a mixing process. On the other hand, dry products based on starches, cellulose, and proteins require a relatively long hydration time and take longer to dissolve than the soluble alkali metal polymers.

U.S. Pat. No. 3,657,175 discloses improved thickening agents based on acrylics, styrene and butadiene, containing bound surfactant groups.

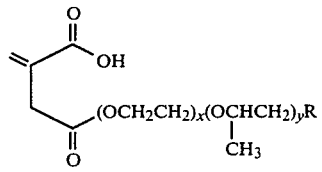
As shown by U.S. Pat. Nos. 4,384,096; 4,351,754, and 4,421,903, improved thickeners for aqueous systems have been developed in which there are introduced to the acrylic polymer backbones ester surfactant groups in sufficient number to enhance thickening and rheological properties. These thickeners find use in paints, coatings, adhesives, cleaners, drilling fluids, textile printing inks, personal care products, and the like.

SUMMARY OF THE INVENTION

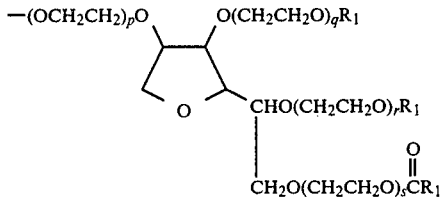
According to this invention, new anionic copolymers are prepared by emulsion copolymerizing (A) an addition copolymerizable substituted methylene succinic acid ester surfactant monomer, (B) an α, β-ethylenically unsaturated carboxylic acid monomer, (C) a nonionic α, β-ethylenically unsaturated monomer, and (D) optionally a small amount of a polyethylenically unsaturated cross-linking monomer. The emulsion polymerization is carried out at a low pH and the resulting copolymers are essentially water insoluble and are present in the aqueous reaction medium in the form of a relatively stable dispersion. Upon addition of an alkaline material to the dispersion to neutralize the residual carboxyl groups on the copolymer, it becomes water soluble and substantially thickens the aqueous system in which it is present. The presence of the copolymerizable substituted methylene succinic ester surfactant monomer imparts to the copolymer the ability to provide higher water viscosities upon neturalization, as well as enhancing electrolyte stability. This latter property is most important to the stability of the rheological properties of thickened aqueous systems of very high alkalinity. The copolymerizable surfactant monomer can easily be prepared in near quantitative yield without unwanted side reactions or formation of by-products which would interfere with production of a commercial product of uniform composition and properties. The reaction employed in preparing the surfactant monomer is general for preparation of all such monomers, and allows the tailoring of copolymers for specific markets.

The new copolymer thickeners are obtained by emulsion polymerizing a monomer system comprising:

(A) about 1 to about 25 percent of at least one methylene succinic acid ester monomer of the formula:

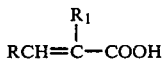


in which x is an integer from 1 to 150, and y is an integer from 0 to 50 when R is alkoxy, alkylphenoxy, dialkyl plenoxy, or alkyl carbonyloxy having 5 to 30 carbon atoms or a sorbitan fatty ester of the formula



where each of p. q, r, and s is an integer and the sum of said integers is from 0 to 100, R_1 is H or COR_2 and R_2 is alkyl, alkyl phenyl, or dialkyl phenyl having 5 to 30 carbon atoms.

(B) about 5 to about 70 percent of a copolymerizable α, β-ethyenically unsaturated carboxylic acid monomer of the formula:



where R is H and R_1 is H, an alkyl group containing from 1 to 4 carbon atoms, or $-CH_2COOX$; R is